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PHYSICAL CHEMICAL PROPERTIES OF METHANE

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PHYSICAL CHEMICAL PROPERTIES OF METHANE[1]

By H. H. Storch[2]

INTRODUCTION

Methane is the chief constituent of natural gas, and large quantities of it are also obtained in coke-oven gas and in the off-gases from cracking higher hydrocarbons. Perhaps the most important potential chemical use of methane is in the production of higher hydrocarbons, both aliphatic and aromatic. The results of a relatively large number of researches have been published in the technical and patent literature on the thermal decomposition of methane, the objective being an industrial process for the production of "antiknock" motor fuel. No industrially feasible process has, however, been developed. An inspection of the literature on this subject indicates that the chief difficulty in the way of accomplishing this object lies in controlling the decomposition so that undesirable products are eliminated. A considerable number of quantitative experiments have been reported, the results of which provide only a vague and confusing picture of the various steps in the thermal decomposition of methane. The reaction mechanism has not been subjected to rigorous fundamental study, and the necessity for such a study is obvious if further progress is to be made.

The thermal decomposition is only one of the reactions of methane which are of potential industrial importance and which require further fundamental investigation. The oxidation, hydrolysis, and halogenation of methane are other reactions which must be studied further. In view of the importance of methane as a raw material for various industrially desirable products, it is appropriate that a survey be made of the important facts concerning the physical and chemical properties of methane which will serve as an aid in subsequent experimental work. No attempt will be made to present a complete chronological review, but rather a condensed critical description of the important literature will be presented.

THERMODYNAMIC PROPERTIES OF METHANE

Keyes, Smith, and Joubert[3] and Keyes and Burks[4] studied the pressure-volume relationship for CH_4 in the pressure range 1 to 300 atmospheres and 273 to 473° Abs. They findthe following equation of state to represent their data accurately:

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6549."

[2] Principal physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Keyes, F. G., Smith, L. B., and Joubert, D. B., The Equation of State for Methane Gas Phase: Jour. Math. and Phys., Mass. Inst. Tech., vol. 1, 1922, p. 191.

[4] Keyes, F. G., and Burks, H. G., The Isometrics of Gaseous Methane. Jour. Am. Chem. Soc., vol. 49, 1927, p. 1403.

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$$p = \frac{5.1173\ (T - y/2)}{v - d} - \frac{9370\ (1 - 0.586\ y)}{v + 0.42}$$

$$\log_{10} d = 0.5611 - 0.978/v$$
$$\log_{10} (v - d)\ \frac{y}{1 - y^2} = \frac{527}{T} - 1.25 \log_{10} T + 0.813$$

where p = pressure in atmospheres and
T = temperature in degrees absolute.

Keyes, Taylor, and Smith[5] measured the vapor pressure of liquid CH_4 from 95 to 191° A., and they present the following equation therefor:

$$\log_{10} p = -\frac{595.546}{T} + 8.09938 - 4.04175 \times 10^{-2}\ T + 1.68655 \times 10^{-4}\ T^2 - 2.51715 \times 10^{-7}\ T^3$$

where p is the vapor pressure in atmospheres, and
T the temperature in degrees absolute.

The boiling point of CH_4 is given by these authors as 111.52° A. By means of the above vapor pressure equation and measurements of the densities of the coexisting phases, Keyes and his coworkers calculated latent heats of vaporization by means of the Clapeyron equation and represented the results by the following equation:

$$\log_{10} L = 1.65214 + 2.0076 \times 10^{-4}(T_c - T) + 0.2225 \log_{10} (T_c - T)$$

where L = heat of vaporization in calories per gram, and
T_c = critical temperature (191.030 A.).

The heat of vaporization at the boiling point (111.52° A.) is, according to this equation, 123 calories per gram or 1968 calories per mol. This figure is considerably at variance with that calculated by the writer from the vapor pressure measurements of Stock, Henning, and Kuss[6] — namely, 2,075 calories per mol. This equation, however, yields 2,104 calories per mol. for the heat of vaporization at the triple point (89.98° A.), which is in excellent agreement with calculations based on the vapor pressure of solid methane as measured by Karwat[7] in the range 76.89 to 87.25° A. and by Freeth and Verschoyle[8] in the range 64.78 to 90.66° A., and on the heat of fusion as given by Clusius.[9] The heat of vaporization of solid methane as calculated from Karwat's measurements is 2,326 calories per mol. which checks very closely with a similar calculation using Freeth and Verschoyle's data. Combining 2,326 calories per mol. with the heat of fusion (at 90.60 A.) of 224 calories per mol. as given by Clusius[9], the value 2,102 calories per mol. is obtained for the heat of vaporization of liquid methane in the vicinity of the melting point. This figure checks that of Keyes, Taylor, and Smith[5] within 0.1 per cent.

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[5] Keyes, F. G., Taylor, R. S., and Smith, L. B, The Thermodynamic Properties of Methane: Jour. Math. and Phys., Mass. Inst. Tech., vol. 1, 1922, p. 211.

[6] Stock, A., Henning, F. and Kuss, E., Dampfdrucktafelen für Temperaturbestimmung zwischen 25° und -185°: Ber. Deut. Chem. Gesell., vol. 54, 1921, p. 1119.

[7] Karwat, F., Die Dampfdruck des festen Chlorwasserstoffs, Methans, und Ammoniaks. Ztschr. Physik. Chem., vol. 112, 1924, p. 486.

[8] Freeth, F. A., and Verschoyle, T. T. H., Physical Constants of the System Methane-Hydrogen: Proc. Roy. Soc. (London) vol. A 130, 1931, p. 453.

[9] Clusius, K., Uber die spezifische Warme Einiger kondensierter Gase zwischen 10° abs. und ihrem Triple punkt: Ztschr. physik. Chem., vol. B 3, 1929, p. 41.

The specific heat of methane from 10.33 to 105.3° A. has been recently measured by Clusius. The specific heat equation given by Eastman[10] for CH_4 may be used in the temperature interval from the boiling point to 298° A. Three determinations of the specific heat in the range 297.7 to 481.2° A. are given by Eucken and Lüde[11], and they are probably more accurate than the data presented by Dixon, Campbell, and Parker[12] which are based on determinations of the velocity of sound in CH_4 at high temperatures. Ludolph[13] presents specific-heat data calculated from theoretical considerations of the structure of the methane molecule. His results are all appreciably lower than any of the experimental data.

A calculation[14] of the entropy of CH_4 based on the specific-heat data outlined in the preceding paragraph yielded the value 43.91 E.U. at 25° C. Calculations of the entropy of CH_4 by way of equilibrium measurements for the reactions:

$$C + 2H_2 \rightleftarrows CH_4 \qquad (1)$$

$$CH_4 + H_2O \rightleftarrows CO_2 + 4H_2 \qquad (2)$$

yielded the values 45.24 and 42.16 entropy units, respectively. Villars[15] computed three values for the entropy of CH_4 from spectroscopic data—namely, 44.1, 42.3 and 42.0, indicating a preference for the last figure. The value 43.91 entropy units calculated from low-temperature specific-heat data is considered by the writer to be the most reliable estimate available at present. A free energy equation based on this entropy figure, and on the heat of combustion of CH_4 recently measured by Rossini[16] using specific heat equations for C, H_2, and CH_4 as indicated elsewhere[17] by the writer, is as follows:

$$\Delta F = -15{,}313 + 10.54\,T\ln T - 4.36 \times 10^{-3}T^2 - 0.11 \times 10^{-6}T^3 - 48.1T$$

CHEMICAL REACTIONS

Methane is a relatively inert gas so far as chemical activity is concerned. This inertness toward chemical change is to be correlated with evidence from ionization potential experiments which indicate that the outer "shell" of the methane molecule consists of 8 electrons similar to the arrangement in the rare gases.[18]. That is to say, the hydrogen atoms are probably inside of an outer shell of 8 electrons. Thus the ionization potential of methane to form CH_4^+ is 14.5 volts and to form CH_3^+ is 15.5 volts,[19] these figures being of the order of magnitude of those for argon and krypton. Oxygen atoms were found by Harteck and Kopsch[20] to react quite rapidly with most organic compounds excepting methane where only a slow reaction was observed. Similarly Bonhoeffer and Harteck,[21] and von Wartenberg and Schultze[22] found that atomic hydrogen would not react with CH_4 to yield any product other than H_2 and CH_4. Ultra-violet light as obtained from a mercury arc lamp does not affect methane,[23] whereas ethane yields H_2, CH_4, C_4H_{10}, C_6H_{14} and other products. In general it may be concluded that the CH_4 molecule is quite resistant to chemical change, necessitating a large energy increment for activation at low temperatures.

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[10] Eastman, E. D., The Specific Heats of Gases at High Temperatures: Tech. Paper 445, Bureau of Mines, 1929, 27 pp.

[11] Eucken, A., and Lüde, K. V., Die Spezifische Waerme der Gase bei mittleren und hohen Temperaturen: Ztschr. physik. Chem., vol. B 5, 1929, p. 436.

[12] Dixon, H. B., Campbell, C., and Parker, A., On the Velocity of Sound in Gases at High Temperatures and the Ratio of the Specific Heats: Proc. Roy. Soc. (London), vol. A 100, 1921, p. 1.

[13] Ludolph, P. C., The Specific Heat of Methane: Phys. Rev., vol. 37, 1931, p. 830.

[14] Storch, H. H., The Free Energy and Entropy of Methane: Jour. Am. Chem. Soc., vol. 53, 1931, p. 1266, gave the value 43.39 entropy units, but an error in calculation of 0.52 units has subsequently been discovered.

[15] Villars, D. S., The Entropy of Polyatomic Molecules: Jour. Am. Chem. Soc., vol. 53, 1931, p. 2006.

[16] Rossini, F. D., The Heats of Combustion of Methane and Carbon Monoxide: Bur. Standards Jour. Research, vol. 6, 1931, p. 37.

[17] See footnote 14.

[18] Glockler, G., The Ionization Potential of Methane: Jour. Am. Chem. Soc., vol. 48, 1926, p. 2021.

THERMAL DECOMPOSITION

A review and bibliography of the thermal decomposition of hydrocarbons, and particularly of methane has been recently published by Egloff, Schaad, and Lowry,[24] and therefore only the more important and more recent data will be presented here.

In static experiments, in which CH_4 was confined in a sealed bulb of quartz or porcelain, it has been found that the decomposition at about 1,000° C. proceeds rapidly at first to carbon and hydrogen, but that the rate decreases practically to zero long before the equilibrium value is reached. Holliday and Exell[25] and Wheeler and Wood[26] postulate that the absorption by the walls of the reaction vessel of the hydrogen produced by the decomposition is responsible for the marked decrease in rate.

A recent paper by Holliday and Gooderham[27] shows conclusively that variation of the surface within wide limits has no measurable effect on the rate of decomposition of methane in quartz bulbs in the temperature range 900 to 1,100°C. These authors suggest that the initial reaction is a homogeneous bimolecular reaction, namely:

$$2\ CH_4 = C_2H_2 + 3\ H_2 \quad - 91{,}000 \text{ calories,}$$

and that this reaction is followed by the decomposition of the acetylene at the surface of the reaction vessel. The apparent equilibria reached after the initially rapid reaction is completed are explained by them as a true equilibrium in the reaction given above for the formation of acetylene from methane; the rate of decomposition of the acetylene being decreased practically to zero due to the adsorption of hydrogen by the surface of the reaction vessel.

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[19] Hogness, T. R., and Kvalves, H. M., The Ionization Process in Methane Interpreted by the Mass Spectrograph: Phys. Rev., vol. 32, 1928, p. 943.

[20] Harteck, P., and Kopsch, U., Gas Reaktionen mit atomarem Sauerstoffe, Ztschr. phys. Chem., vol. B 12, 1931, p. 327.

[21] Bonhoeffer, K. F., and Harteck, P., Über die Reaktionen von atomaren Wasserstoff mit Kohlenwasserstoffen: Ztschr. physik. Chem., vol. 139, 1928, p. 64.

[22] von Wartenberg, H., and Schultze, G., Die Einwirkung atomaren Wasserstoffes auf Kohlenwasserstoffe, Ztschr. physik. Chem., vol. B 2, 1929, p. 1.

[23] Kemula, W., Action of Ultra-Violet Rays on Aliphatic Hydrocarbons: Chem. Abs., vol. 24, 1930, p. 4462.

[24] Egloff, G., Schaad, R. E., and Lowry, C. D., Jr., The Decomposition of the Paraffin Hydrocarbons: Jour. Phys Chem., vol. 34, 1930, p. 1617.

[25] Holliday, G. C., and Exell, H. C., The Thermal Decomposition of Methane. Part I. Decomposition in Silica Bulbs: Jour. Chem. Soc. (London), 1929, p. 1066.

[26] Wheeler, R. V., and Wood, W. L., Recent Experiments on the Pyrolysis of Methane: Fuel in Sci. and Practice, vol 9, 1930, p. 567.

[27] Holliday, G. C., and Gooderham, W. J., The Thermal Decomposition of Methane. Part II - The Homogeneous Reaction: Jour. Chem. Soc. (London), 1931, p. 1594.

The mechanism suggested by Holliday and Gooderham is seen to be highly improbable, if one calculates the theoretical rate of the reaction (requiring at least 91,000 calories for activation) assuming that every collision between two methane molecules, which can supply the necessary energy of activation, is effective. Such a calculation (made by L. S. Kassel, associate physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines) shows that the theoretical rate is approximately 10^5 times smaller than the actual rate.

In dynamic experiments varying yields of acetylene, ethylene, benzol, tar, and carbon are reported, the most important variables being the time of contact within the hot zone and the temperature. The character of the walls of the reaction tube exerts little or no influence on the reaction, provided strongly "methanizing" metals such as iron, nickel, cobalt, etc., are avoided. The latter catalyze the production of carbon and hydrogen. Quartz, porcelain, and copper are the materials commonly employed. Wheeler and Wood[28] find that dilution with nitrogen had only a slight effect on the yield of aromatic hydrocarbons at 1,000° C. using relatively long times of contact (1 to 2 minutes) in a quartz tube, whereas dilution with hydrogen results in markedly decreased yields. In a later paper[29] the same authors working at 1,050° C. in quartz tubes conclude that the important variable is the time of contact, rather than the surface exposed to the CH_4. This is illustrated by the data of Table 1 which also includes some data on the use of a chrome-iron reaction tube.

Table 1.- Wheeler and Wood's data on relative importance of time of contact and surface to volume ratio at 1,050° C. using 96 per cent of CH_4

Material	Surface to volume ratio	Time of contact, seconds	CH_4 decomposed to $C + 2H_2$, per cent	CH_4 converted to liquid products, per cent	CH_4 converted to higher hydrocarbons (mainly two carbon atoms), per cent
Quartz	1.86	11.2	45.5	8.1	10.3
		6.2	39.3	12.2	11.9
		4.3	32.6	15.0	16.6
		3.3	27.5	18.7	19.0
		2.6	22.6	18.2	24.3
Quartz	27.00	3.7	28.15	13.0	13.6
		1.6	18.21	15.2	22.0
		0.6	6.08	25.6	45.0
		0.45	4.06	15.0	61.3
		0.3	2.48	12.7	71.5
Chrome-iron	1.6	9.0	43.1	6.7	9.1
		4.5	33.5	9.8	13.7
		3.25	27.1	12.0	20.0
		2.5	18.1	12.1	31.9
		2.0	11.8	10.8	46.5

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[28] Wheeler, R. V., and Wood, W. L., The Pyrolysis of Methane: Fuel in Sci. and Practice, vol. 7, 1928, p. 535.

[29] See footnote 26.

Wheeler and Wood found little or no acetylene or propylene in the decomposition products but butylene and butadiene were present in appreciable amounts.

The results of Fischer, et al,[30] are in substantial agreement with those of Wheeler and Wood. Stanley and Nash[31] report their maximum yields (using quartz tubes at 1,100° C., pure CH_4 at atmospheric pressure) of light oil, and tar were obtained with about 1 second contact time. Their off-gases contained about 1 per cent acetylene and about the same percentage of ethylene. Fischer and Meyer[32] report 5.9 per cent of C_2H_2 in their off-gases when using 760-millimeters pressure, 1,200 to 1,550° C., and 0.02 to 0.0003 second contact time with an electrically heated tungsten wire. At 50-millimeters pressure and 1,300 to 3,000° C., 9 to 15 per cent of C_2H_2 was obtained at 0.0005 to 0.0001 second contact time. The tungsten wire deteriorated rapidly, because of carbon deposition. Unfortunately, no details concerning the other constituents of the off-gas are given.

Frolich, White, and Dayton[33] working at about 1,100° C. and 30 to 40 millimeters of Hg pressure, obtained a maximum C_2H_2 content of about 6.5 per cent in the off-gases, the time of contact being about 0.05 seconds. The off-gas containing 6.5 per cent of C_2H_2 also contained about 6 per cent of H_2. Theoretically the H_2 content should have been at least three times that of C_2H_2. It is possible that some H_2 may have been lost by diffusion through the quartz tube. The authors also find that the C_2H_2 yield is very sensitive to the time of contact and the pressure. The percentage of C_2H_2 found did not vary much with either time of contact or pressure, but remained approximately constant at 1.5 to 2.0 per cent. The amount of carbon, tar, and oil formed decreased rapidly with decrease in pressure and time of contact.

De Rudder and Biedermann[34] have done a most careful and complete research in so far as the production of acetylene by the pyrolysis of methane is concerned. They performed their experiments in quartz, at temperatures of 900 to 1,500° C. and pressures of 760 millimeters to 34 millimeters of Hg, using 99.7 per cent of CH_4, 0.3 per cent of N_2 as raw material. Their results are of sufficient importance to reproduce here in Table 2. Only very small amounts of tar and oil were obtained at 1,000° C. Above this temperature little or no tar or oil was observed.

The results of Table 2 show that the maximum C_2H_2 content was obtained at 1,200° C. using 100-millimeters pressure and 2.0 seconds contact time; and the maximum C_2H_2 content at 1,500° C., 44 millimeters pressure, and 0.013 second contact time. In the latter experiment 52.5 per cent of the CH_4 was converted mainly to C_2H_2 and only 10.5 per cent to carbon, 37 per cent being recovered unchanged.

The results given in Table 2 indicate that ethylene is the primary product of the thermal decomposition, rather than acetylene. Thus at 1,000°C. little if any acetylene is present, whereas the ethylene content is of the order of 1 to 2 per cent, and is increasing with decreasing time of contact. Similarly at 1,300° C. the ethylene content increases from 0.6 per cent to 1.7 per cent when the time of contact is changed from 0.51 to 0.05 second, respectively, whereas the acetylene content decreases from 6.6 per cent to 2.7 per cent with the same change of contact time.

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[30] Fisher, F., Pichler, H., Meyer, K., and Koch, H., The Formation of Benzol and other Hydrocarbons by the Action of Heat on Methane: Brenn Chem., vol. 9, 1928. p. 309; 2nd. Internat. Conference on Bit. Coal. vol. 2, 1928. p. 789.

[31] Stanley, H. M., and Nash, A. W., The Production of Gaseous, Liquid and Solid Hydrocarbons from Methane. Part I - The Thermal Decomposition of Methane: Jour. Soc. Chem. Ind., vol. 48, 1929, p. 1, T.

[32] Fisher, F . and Meyer, K., Über die thermische Bildung von Acetylen aus Methan: Brenn. Chem., vol. 10, 1929. p.324.

[33] Frolich, P. K., White, A., Dayton, H. P., Studies on Production of Acetylene from Methane. I - Cracking Under Vacuum: Jour. Ind. Eng. Chem., vol. 22, 1930, p. 20.

[34] Rudder, Fr. de, and Biedermann, H., Sur la pyrogenation du Methane: Compt Rend., vol. 190, 1930, p. 1194; Bull. Soc. Chim., vol. 47, 1930, p. 710.

Table 2.- Results of Rudder and Biedermann's experiments on thermal decomposition of methane

Temp., °C.	Time of contact, seconds	Pressure, millimeters of Hg	Per cent in off-gases of				Per cent conversion of CH_4 to		Per cent of CH_4 undecomposed
			CH_4	H_2	C_2H_2	C_2H_4	C	C_2H_2	
900	75.0	760	84.8	8.9	0.2	1.6	3.0	4.0	93.0
1000	0.7	87	–	3.8	–	0.2	3.5	0.5	96.0
1000	4.9	760	83.4	14.0	0.5	1.7	5.0	4.0	91.0
1000	15.8	760	42.1	55.1	–	1.8	36.0	5.0	59.0
1000	58.0	760	34.7	64.0	–	0.9	46.0	2.0	52.0
1200	0.36	53	–	6.55	–	0.9	2.5	2.5	95.0
1200	0.8	81	–	13.0	–	2.2	4.5	4.5	91.0
1200	2.0	105	–	29.0	2.3	3.4	9.0	14.0	77.0
1300	0.05	151	64.4	27.4	2.7	1.7	9.0	11.0	80.0
1300	0.14	118	33.6	57.1	6.0	0.9	28.5	21.0	50.5
1300	0.51	142	13.8	76.1	6.6	0.6	49.0	26.0	25.0
1400	0.043	134	17.8	73.6	5.6	0.1	48.0	20.0	32.0
1400	0.10	82	21.7	55.9	11.0	1.5	17.5	44.0	38.5
1400	0.13	34	21.9	63.5	10.6	0.9	25.0	38.0	37.0
1500	0.007	60	52.7	34.2	6.7	3.3	4.5	26.0	70.6
1500	0.013	44	21.5	59.4	14.85	1.3	10.5	52.5	37.0
1500	0.2	73	2.2	30.6	14.4	–	37.0	58.2	4.54

The work of Hague and Wheeler[35] also indicates that ethylene is the parent substance for the formation of benzol; the intermediary stages being butylene, butadiene, and hexadiene. Naphthalene may be formed by way of the condensation of butadiene with benzol, and anthracene from naphthalene and butadiene.

Wheeler[36] subjected the work of Bone and Coward,[37] Wheeler and Wood,[38] and Holliday and Exell[39] to an analysis based on the assumption that in both the static and streaming experiments the reaction was entirely heterogeneous, hydrogen exercising a marked retarding influence. The curves given by Bone and Coward and Wheeler and Wood indicate that in static experiments after the first rapid decomposition has ceased, a reaction of zero order (amount of methane decomposed per unit time is constant and independent of its pressure) becomes apparent. Holliday and Exell's results, however, do not supply any evidence for such zero order reaction. Wheeler develops rate equations of the type:

$$- dp/dt = k_1 p^n \quad (1 - k_2 \{ (P - p)^a / p \}^b),$$

where p is the pressure of CH_4 at time t, and is calculated from the initial pressure P and the observed total pressure 2 P - p at time t. p indicates the order of the reaction as regards CH_4. k_1 is the velocity constant for the particular reaction vessel used, and $k_2\ ((P - p)^a/p)^b$ represents the retarding influence of hydrogen. In all cases Wheeler puts $n = 1$, and for Holliday and Exell's results $a = 2$, $b = 0.25$, whereas for the other investigators $a = 3$, $b = 1/9$. While these equations represent the results with fair accuracy, the author (Wheeler) states that no physicochemical interpretation of them can be given at present. Heats of activation between 30,000 and 34,000 calories are calculated by Wheeler.

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[35] Hague, E. N., and Wheeler, R. V., The Mechanism of Thermal Decomposition of the Normal Paraffins: Jour. Chem. Soc. (London), 1929, p. 378.

[36] Wheeler, T. S., The Kinetics of the Thermal Decomposition of Methane: Fuel, vol. 10, 1931, p. 175.

[37] Bone, W. A., and Coward, H. F., The Thermal Decomposition of Hydrocarbons: Jour. Chem. Soc., vol. 93, 1908, p.1197.

[38] See footnotes 26 and 28.

[39] See footnote 25.

This complexity of the retardation of CH_4 decomposition by hydrogen is not without parallel, for Hinshelwood[40] cites a similar case—namely, the decomposition of NH_3 on quartz. He states:

> In the equation $dx/dt = (k(a - x))/(1 + bx)$, the factor $1/(1 + bx)$, which represents the retarding effect, reduces as we have seen to $1/bx$ for large values of b and becomes equal to unity when b vanishes. For intermediate conditions it may be represented approximately by an inverse fractional power of x. This is the origin of the relation sometimes found empirically that the retarding effect of a gas is proportional to the square root of its pressure.

It will be observed that Wheeler's equation when $n = 1$, $a = 2$, and $b = 0.25$, presents just this proportionality of the retarding effect.

The writers chief criticism of Wheeler's paper concerns the assumption that in the streaming experiments the reaction is entirely heterogeneous. If this were the case, it would be very difficult to account for the observation by several experimenters that a large increase in the surface exposed to the CH_4 does not alter the reaction rate appreciably. This indicates that while the reaction may be initiated at the walls, it is probably largely homogeneous after it is once started. A chain reaction with long chains is also ruled out, for in this case the rate would be decreased by increased surface exposure.

The primary steps in the thermal decomposition of methane are as yet quite obscure. The following series of reactions should, however, be considered in any experiments on the primary steps:

$$CH_4 + \text{hot quartz or hot carbon} \rightarrow C + 2H + H_2 \qquad (1)$$
$$CH_4\ (\text{adsorbed}) + H\ (\text{adsorbed}) \rightarrow CH_3 + H_2 \qquad (2)$$
$$CH_3 + CH_4 \rightarrow C_2H_5 + H_2 - 11{,}000 \text{ cals.} \qquad (3)$$
$$C_2H_5 \rightarrow C_2H_4 + H - 20{,}000 \text{ cals.} \qquad (4)$$
$$CH_3 \rightarrow CH_2 + H - 25{,}000 \text{ cals.} \qquad (5)$$
$$CH_2 + CH_4 \rightarrow C_2H_4 + H_2 + 20{,}000 \text{ cals.} \qquad (6)$$
$$CH_4 + H \rightarrow CH_3 + H_2 - 25{,}000 \text{ cals.} \qquad (7)$$

The first step is the complete dissociation of methane to form a layer of carbon atoms on the surface of the reaction vessel. The hydrogen resulting from the decomposition may be partially adsorbed as monatomic hydrogen on the carbon atoms, and the remainder as molecular hydrogen. The second step consists in the reaction of adsorbed methane with adsorbed monatomic hydrogen to form a methyl radical and molecular hydrogen. The heat of formation of molecular hydrogen is somewhat less than that necessary to break an $H_3C - H$ bond, and hence the reaction is only mildly exothermic. Some energy of activation may be necessary to activate the methane.

It is probable that as soon as atomic hydrogen is present due to reactions (4) and (5) the synthesis of ethylene will be a homogeneous chain reaction. The chains will, however, be very short, due to the continuous removal of atomic hydrogen by the walls of the reaction

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[40] Hinshelwood, C. N., Kinetics of Chemical Change in Gaseous Systems: Oxford, 1929, 2nd ed., p. 209.

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vessel. The effect of increased surface exposure can not be readily predicted, for while the rates of reactions (1) and (2) would be increased, the rate of reactions (7) would be decreased because of the recombination of hydrogen atoms at the surface to form molecular hydrogen.

The heats of reaction listed in reactions (3) to (7), inclusive, are approximations based on the estimates of Mecke[41]. The probability of reaction (4) has recently been discussed by Rice.[42]

EFFECT OF ELECTRIC DISCHARGE THROUGH METHANE

Egloff, Shaad, and Lowry[43] present a comprehensive review of research on the electrical decomposition of methane up to early in 1930. At that time the most interesting results from a practical point of view were those of Fischer and Peters[44] who were able to obtain 82.3 per cent conversion of CH_4 to acetylene by passing coke-oven gas through an electrical discharge tube at about 50 millimeters pressure. The electrodes were of Krupp V 2A steel and about 50 centimeters apart, about 2,000-volts, 50-cycle current being employed. The energy required per cubic meter of acetylene was 31 kilowatt-hours. Subsequently Peters and Pranschke[45] showed that in passing 1160 liters per hour of a gas (containing 54.6 per cent of H_2, 24.9 per cent of CH_4, 9.7 per cent of N_2, 2.1 per cent of CO_2, and 0.9 per cent of O_2) through an electric discharge tube (5-centimeter diameter electrodes 30 centimeters apart) at 40 to 60 millimeters Hg pressure, the off-gas contained 8.0 per cent of C_2H_2; no carbon was deposited, and the energy consumption was 11.6 kilowatt-hours per cubic meter of acetylene produced. This corresponds to about 30 per cent conversion of the CH_4. At lower pressures (10 to 20 millimeters) a much higher conversion—namely, about 95 per cent of CH_4 to acetylene is claimed.

As reported in a later paper, Peters and Wagner,[46] using a gas containing 91.9 per cent of CH_4, 3.4 per cent of N_2, 3.5 per cent of H_2, and 0.9 per cent of $(O_2 + CO)$ at about 90 millimeters pressure and 0.05 second contact time, obtained a minimum energy value of 13 kilowatt-hours per cubic meter of acetylene, the product containing 4.2 per cent of C_2H_2. Low concentrations (about 0.8 per cent) of ethylene were also obtained. Dilution with hydrogen favors the conversion of CH_4 to acetylene up to a maximum when the ratio of CH_4 to H_2 is 2 : 1. At lower pressures (that is, less than 10 millimeters) appreciable amounts of C_2H_6 and C_3H_8 appeared in the off-gases. The minimum energy consumption per cubic meter of acetylene produced for any given set of conditions (that is, space velocity and pressure particularly) is obtained when the power input is increased just to the point where the color of the discharge changes from blue to yellow. This change is associated with the appearance of a new carrier—namely, C_2 ions. It is not possible at this time to present a detailed picture of the mechanism of the production of acetylene from CH_4 by electric discharge, especially since Eisenhut and Conrad[47] have shown by mass spectrographic methods that every species of ion from one to four carbon atoms is present in the discharge.

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[41] Mecke, R., Experimentelle Ergebnisse und Ziele der Bandenforschung: Ztschr. Elektrochem., vol. 36, 1930, p. 595.

[42] Rice, F. O., The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. I - Saturated Hydrocarbons: Jour. Am. Chem. Soc., vol. 53, 1931, p. 1959.

[43] See footnote 24.

[44] Fischer, F., and Peters, K., Über die Einwirkung Elektrischen Entladungen auf Kohlenwasserstoffhaltige Gase bei Vermindertem Druck: Ztschr. physik. Chem., vol. A 141, 1929, p. 180.

Fischer, F., and Peters, K., Über die Umwandlung von Methan bzw. Koksofengas durch Elektriche Entladungen bei Unterdruck: Brenn. Chem., vol. 10, 1929, p. 108.

[45] Peters, K., and Pranschke, A., Neue Versuche über die Umsetzung von Methan aus Koksofengas in Acetylen durch Elektrische Entladungen: Brenn. Chem., vol. 11, 1930, p. 239.

[46] Peters, K., and Wagner, O. H., Athylen - und Acetylenbildung aus Methan in Elektrischen Entladungen: Ztschr. physik. Chem., vol. A 153, 1931, p. 161.

In the recently published work of Brewer and Kueck[48] on the decomposition of methane in the glow discharge using much lower voltages (several hundred volts) and pressures (a few millimeters of mercury) than Fischer and his coworkers and immersing the discharge tube in liquid air, practically quantitative conversion of methane to ethylene was obtained. These authors suggest that the reaction is essentially the following:

$$(CH_4)^+ + CH_4 \rightarrow (C_2H_4)^+ + H_2 ,$$

the $(C_2H_4)^+$ being rapidly freed of its electric charge by neutralization at the walls of the discharge tube. The fact that in both the thermal decomposition of and electric discharge through CH_4, ethylene appears to be one of the earliest products is perhaps signigicant, but at present it can be regarded only as a coincidence with little or no bearing on the mechanism of the two systems of reaction.

OXIDATION OF METHANE

Egloff and Schaad[49] have reviewed the literature on the oxidation of methane up to 1929. The main objective of most of the research work on this subject has been to obtain an industrially feasible process for the production of formaldehyde. Since the production of cheap methanol from water gas, the search for such a process has practically ceased, because of the ease with which formaldehyde can be produced from methanol.

The kinetics of the oxidation of methane has been studied by Pease and Chesebro[50] and more recently by Fort and Hinshelwood[51]. The oxidation is apparently a chain reaction, for the rate is decreased by an increase in the surface exposed to the reactants.

The relation between the rate and concentrations of methane and oxygen is of no simple order, the nearest integral value being 3 or 4. The rate increases rapidly with increasing CH_4 concentration but is relatively little influenced by the O_2 concentration. An induction period exists in the oxidation of CH_4, during which the rate of reaction is low. Fort and Hinshelwood state that this induction period probably represents the time necessary for the production of the "steady state" concentration of formaldehyde, for a similar induction period exists in the oxidation of methanol.

The partial oxidation of methane using $2CH_4 + 1\ O_2$ and producing a mixture of water gas and acetylene was studied by Fischer and Pichler[52]. The results of this work are given in the following table.

The mixture of water gas and acetylene as obtained in the experiments of Table 3 would probably give a considerably higher yield of gasoline when passed over proper catalysts at about 200° C., than is obtained with water gas alone.

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[47] Eisenhut, O., and Conrad, R., Beobachtungen ber Zerfall und Bildung von Kohlenwasserstoffen in Entladungsröhren mit hilfe von Kanalstrahlen: Ztschr. Elektrochem, vol. 36, 1930, p. 654.

[48] Brewer, A. K., and Kueck, P. D., Chemical Action in the Glow Discharge. VII - Dissociation and Oxidation of Methane: Jour. Phys. Chem., vol. 35, 1931, p. 1293.

[49] Egloff, G., and Schaad, R. E., The Oxidation of the Paraffin Hydrocarbons: Chem. Rev., vol. 6, 1929, p. 91.

[50] Pease, R. N., and Chesebro, P. R., Characteristics of Homogeneous Exothermic Gas Reactions: Proc. Nat. Acad. Sci., vol. 14, 1928, p. 472.

[51] Fort, R., and Hinshelwood, C. N., Further Investigations on the Kinetics of Gaseous Reactions: Proc. Roy. Soc., vol. A. 129, 1930, p. 284.

[52] Fischer, F., and Pichler, H., Über die Partielle Verbrenung von Methan bei Verschiedenen Drucken, mit besondere Berucksichtigung der hierbei auftretenden Acetylenbildung: Brenn. Chem., vol. 11, 1930, p. 501.

Table 3.- Partial oxidation of methane by oxygen

2.5 by 100 millimeter Pythagorasmasse tube 105
liters per hour of $2CH_4 + 1\ O_2$ for 5 hours
at 1,150 to 1,200° C.

	Volume, per cent							
	CO_2	C_2H_2	O_2	CO	H_2	CH_4	C_2H_6	N_2
Reactants	0	0	33.6	1.8	0.4	59.4	0.0	4.8
Products	2.5	9.5	0.2	23.5	50.9	10.0	0.0	3.4
	Also 20 c. c. of "light oil."							
$CH_4 + O_2$ passed through 2.5 by 100 millimeter tube at 1,400° C.								
O_2 liters/hour	0	20	30	40	50	60	70	80
$O_2 + CH_4$ liters/hour	109	136	150	156	174	183	204	234
CO_2, volume, per cent	0.2	0.9	1.6	1.4	2.4	3.0	3.0	3.4
C_2H_2 do	5.2	7.6	8.2	9.0	9.4	9.4	6.6	1.2
O_2 do	0.3	0.5	0.6	0.2	0.0	0.0	0.0	0.2
CO do	1.2	12.4	16.3	19.6	22.7	25.8	30.4	35.8
H_2 do	25.5	38.6	44.5	48.5	53.1	54.2	56.3	56.4
CH_4 do	64.3	37.0	25.8	18.6	9.4	4.8	1.9	0.8
CH_4 to C_2H_2 do	12.2	21.4	26.6	30.4	34.8	37 0	29.4	5.0

Bone[53] has recently found that the direct oxidation of methane, using a mixture of $9\ CH_4 + 1\ O_2$ at 360° C. and 100 atmospheres pressure, yielded considerable quantities of (17 per cent of the CH_4 reacting to form) methanol, the bulk of the products being CO, CO_2 and H_2O.

REACTION OF METHANE WITH STEAM AND CARBON DIOXIDE TO PRODUCE WATER GAS

The production of water gas by way of the hydrolysis of methane is an exothermic reaction which requires a temperature of about 1,000° C. for practically complete conversion of the methane. About the same temperature is essential for the reaction with carbon dioxide. Fisher and Tropsch[54] investigated the activity of a variety of materials as catalysts for the CO_2 reaction. Copper, iron, Mo, and W were found to have little or no catalytic activity at 850° C., whereas CO or Ni promoted with Al_2O_3 is an excellent catalyst. Hawk. Golden, Storch, and Fieldner[55] found Co to be a much poorer catalyst than Ni for the H_2O reaction They obtained high conversions using a Ni catalyst prepared by impregnating an Al_2O_3 + clay refractory (corundite) with $Ni(NO_3)_2$ solution and subsequently reducing to metallic nickel. Their process consists of alternately blasting the catalyst-filled converter with $CH_4 + O_2$ and then $CH_4 + H_2O$. Purging after the heating blast is of course essential to remove N_2, CO_2, etc.

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[53] Bone, W. A , Formation of Methyl Alcohol by Direct Oxidation of Methane: Nature, vol. 127, 1931, p. 481.

[54] Fischer, F., and Tropsch, H., Die Umwandlung von Methan in Wasserstoff und Kohlenoxid. Brenn. Chem. vol. 9, 1928, p. 39.

[55] Hawk, C. O., Golden, P., Storch, H. H., and Fieldner, A. C., The Conversion of Methane to Carbon Monoxide and Hydrogen: Ind. and Eng. Chem To be published.

Gluud, Klempt, Brodkort, et al.,[56] found it possible to use an alloy tube (20 per cent of Ni, 25 per cent of Cr, 55 per cent of Fe) and external heating, on the catalytic (Ni on burned dolomite or on Al_2O_3) hydrolysis of methane. There was, however, a slow, but continuous loss in weight by the alloy tube.

Peters and Pranschke[57] studied the reaction of methane with H_2O and CO_2 in the electric discharge. At 50 millimeters pressure they obtained quantitative conversion to CO + H_2 when the current density was sufficiently high. At lower current densities varying quantities of acetylene were obtained. Their most interesting result was the conversion of a mixture of $1CO_2 + 2CH_4$ into a gas which contained 26.1 per cent of CO, 53.3 per cent of H_2, 10.0 per cent of C_2H_2, 4.7 per cent of CO_2, 3.6 per cent of CH_4, and 1.04 per cent of higher hydrocarbons. Such a product would be excellent raw material for gasoline production.

The catalytic hydrolysis of methane at high pressures and at 250 to 500° C. is claimed by Dreyfuss[58] to yield methanol and higher alcohols.

REDUCTION OF METALLIC OXIDES BY METHANE

The use of methane (or natural gas) for metallurgical purposes, has received comparatively little attention. Bouton[59] studied the reduction of hematite to magnetite by methane-hydrogen mixtures and found the methane reaction to be slow. Thus even at 900° C. the time of contact required for 90 per cent utilization of the methane was 34 seconds. Thermodynamic calculations made by the writer indicate that it may be possible to reduce either hematite or magnetite to metallic iron by methane without carbon deposition if a reaction temperature above 650° C. is employed. Below this temperature carbon deposition is practically certain to occur, whereas above it some temperature may be found at which a sufficiently rapid rate of reduction combined with little or no carbon deposition is obtained. Preliminary experiments by the Bureau of Mines indicate that about 900° C. is essential for a sufficiently rapid reaction rate, and that if methane free from higher hydrocarbons is used, little or no carbon deposition occurs. The reductions of both hematite and magnetite are endothermic, and 1,500 to 2,000 B.t.u. (depending upon the character of the ore and the temperature of reduction) must be supplied per pound of metallic iron produced.

The reduction of zinc oxide by methane was subjected to a thermodynamic analysis by C. G. Maier[60] who found 870° C. to be the minimum temperature necessary to avoid carbon deposition. Subsequent experimental work by Doerner[61] showed that in the temperature range 975 to 1,000° C. little or no carbon is deposited and the rate of reduction of zinc oxide and vaporization of zinc metal is sufficiently rapid to compare favorably with that obtained from retorts by standard practice. The metal produced is of exceptional purity.

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[56] Gluud, G., Klempt, W., Brodkort, F., et al., Ber. Ges. für Kohlentechnik mb.H. "Wasserstoff Heft". vol. 3, 1930, pp. 211-370.

[57] Peters, K., and Pranschke, A., Die Umsetzung des Methans mit Kohlendioxid und Wasserdampf in Elektrischen Entladungen: Brenn. Chem., vol. 11, 1930, p. 473.

[58] Dreyfuss, -.: French Patent 698,094, June 26, 1930.

[59] Bouton, C. M., The Rate of Reduction of Hematite to Magnetite by Methane: Rept. of Investigations 2381, Bureau of Mines, 1922, 9 pp.

[60] Maier, C. G., Zinc Smelting from a Chemical and Thermodynamic Viewpoint: Bull. 324, Bureau of Mines, 1930, 93 pp.

[61] Doerner, H. A., Reduction of Zinc Oxide by Methane or Natural Gas: Rept. of Investigations 3091, Bureau of Mines, 1931, 14 pp.

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Experiments on the reduction of copper and cobalt oxides by methane are reported by Campbell and Gray.[62] Carbon dioxide and water are the chief products in the temperature range studied—namely, 300 to 650° C.

SYNTHESIS OF HYDROGEN CYANIDE FROM METHANE AND AMMONIA

Hydrogen cyanide has for a long period of years been produced by the treatment of sodium cyanide with sulphuric acid. In recent years the synthesis of formamide from CO and NH_3 has led to experimentation on the catalytic dehydration of formamide to produce HCN. Research on the synthesis of HCN directly from CO and NH_3 has also received the attention of Bredig, Elöd, at al.[63,64,65] The best yield obtained by these experimenters was when using a twentyfold excess of CO at 700° C. and a cerium oxide-alumina catalyst; 65 per cent conversion of NH_3 to HCN with 14 per cent loss of NH_3 by decomposition. The synthesis of HCN from hydrocarbons and ammonia by the use of contact catalyst was investigated by Bredig, Elöd, and Demme.[66] The yields with equimolar mixtures of NH_3 with CH_4, C_2H_2, and C_2H_4 were as follows:

Table 4.- Formation of HCN from hydrocarbons

Reactants	Catalyst	Temp., °C.	NH_3 converted to HCN, per cent	NH_3 lost by decomposition, per cent
$NH_3 + C_2H_4$	$SiO_2 + Al_2O_3$	800	71.5	19.5
$NH_3 + C_2H_2$	Al_2O_3	800	40.0	23.6
$NH_3 + CH_4$	Al_2O_3	1000	10.7	89.3

The reaction of methane with ammonia to form HCN appears to proceed by way of acetylene or ethylene for no appreciable quantities of HCN are formed until temperatures close to 1,000° C. are employed.

Fischer and Peters[67] found that when an excess of nitrogen is added to CH_4 and the mixture passed through an electric discharge (about 5,000 volts for 40 centimeters electrode distance), the methane is practically completely converted to HCN. Subsequently Peters and Küster[68] studied the reaction between methane and ammonia in the electric discharge. They used a 5 by 75 centimeter tube containing electrodes of Krupp V2A steel 40 centimeters apart.

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[62] Campbell, J. R., and Gray, T., The Influence of various Catalysts in Promoting the Oxidation of Metnane by Means of Copper Oxide: Jour. Soc. Chem. Ind., vol. 49, 1930, p. 447.

[63] Bredig, G., Elöd, E., and Müller, Rudolf K., Zur Kenntnis der Katalytischen Blausaurebildung. Part III - Blausaure bildung aus Kohlenoxyd und Ammoniak: Ztschr. Elektrochem., vol. 36, 1930, p. 1003.

[64] Bredig, G., Elöd, E., and Kortüm, G., Zur Kenntnis der Katalytischen Blausaurebildung. Part IV. Blausaurebildung aus Kohlenoxyd und Ammoniak: Ztschr. Electrochem., vol. 36, 1931, p. 1007.

[65] Bredig, G., Elöd, E., and König, Walter, Zur Kenntnis der Katalytischen Blausaurebildung. Part V - Über Ceroxyd als Katalysator bei der Blausaurebildung: Ztschr. Elektrochem., vol. 37, 1931, p. 2.

[66] Bredig, G., Elöd, E., and Demme, Ernst, Zur Kenntnis der Katalytischen Blausaurebildung. Part II - Blausaurebildung aus Kohlenwasserstoffen und Ammoniak: Ztschr. Elektrochem, vol. 36, 1930, p. 991.

[67] See footnote 44.

[68] Peters, K., and Küster, H., Blausaurebildung in Elektrischen Entladungen: Brenn. Chem., vol. 12, 1931, p. 122.

One phase of 220-volt 50-cycle current was fed to a 220/10,000 volt transformer to furnish high-voltage current. They found that at 120 liters per hour of flow of $1CH_4 + 1NH_3$ at 20 to 40 millimeters pressure and an energy consumption of 2.0 kilowatts, about 70 per cent of the CH_4 was converted to HCN with 23.5 per cent loss of NH_3. In this experiment the highest power input investigated by them was employed, and it is probable that higher conversions can be obtained with higher current densities. The following table shows their results on the influence of the ratio of CH_4 to NH_3, the experiments being conducted in the apparatus described above, and the gas flow being about 120 liters per hour in each case.

Table 5.- Influence of CH_4/NH_3 ratio on HCN production by electric discharge

Experiment No.	CH_4, per cent	NH_3, per cent	Voltage	Pressure, mm.Hg	CH_4 converted to HCN, per cent	NH_3 converted to HCN, per cent	CH_4 converted to C_2H_2, per cent	NH_3 decomposed, per cent	Higher hydrocarbons in off gas,[1] per cent
11	30	70	6460	35	90.3	38.7	3.9	62.4	0.3
5	50	50	5820	30	66.6	66.7	18.1	23.4	3.2
7	50	50	5640	23	69.7	69.7	17.1	23.5	2.7
9	70	30	5820	27	38.0	88.9	48.0	9.4	9.6
10	85	15	5640	28	22.2	100.0	58.7	0.0	12.8

[1] Mainly acetylene.

Experiment No. 10 is of special interest, for combined with complete conversion of NH_3 to HCN, 58.7 per cent of the CH_4 is obtained as acetylene.

HALOGENATION OF METHANE

The data on the reactions of methane and of other hydrocarbons with the halogens has been very recently summarized by Egloff, Schaad, and Lowry[69] so that it is unnecessary to review such literature here. Our knowledge of the chemistry of the halogenation of methane is in a much more satisfactory state than any other of its reactions, although there is ample opportunity for further research, as indicated by Egloff, et al.

SUMMARY

A brief critical review of the more important data on the physical and chemical properties of methane is presented, the primary object being to provide an introduction to further research on the utilization of waste natural gas. Perhaps the most interesting section of this review concerns the thermal decomposition of methane. Some suggestions concerning the mechanism of this decomposition are presented. The first section of the paper presents the thermodynamic properties of methane, and subsequent sections discuss the thermal and electrical decompositions, the oxidation by oxygen, carbon dioxide, and metal oxides, the hydrolysis by steam, and the synthesis of hydrogen cyanide in the electric discharge from methane and nitrogen.

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[69] Egloff, G., Schaad, R. E., and Lowry, C. O., jr., Halogenation of the Paraffin Hydrocarbons: Chem. Rev., vol. 8, 1931, p. 1.